REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE

22 March 94

3. REPORT TYPE AND DATES COVERED

Final Report

4. TITLE AND SUBTITLE

Development of a Jet-Type Singlet Oxygen Generator

5. FUNDING NUMBERS

F6170893W0892

6. AUTHOR(S)

Professor Salman Rosenwaks

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Ben-Gurion University of the Negev
Physics Department
PO Box 653
Beer-Sheva 84105 Israel

8. PERFORMING ORGANIZATION REPORT NUMBER

SPC-93-4062

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

EOARD
PSC 802 BOX 14
FPO 09499-0200

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

SPC-93-4062

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

A

13. ABSTRACT (Maximum 200 words)

Under the framework of the contract, we have carried out experimental and theoretical investigations of small-scale jet singlet oxygen generators (SOG) of the type described in the Soviet Journal of Quantum Electronics, Vol 21, p. 747, 1991.

The present experimental studies have shown that jet-type generator can operate at high pressures, up to 40 Torr. The maximum $O_2(^1\Delta)$ yield was achieved at 17 Torr; assuming complete chlorine utilization, the yield was 40 $\pm$ 15%. The yield dropped at higher pressures, to 25 $\pm$ 10%, at 40 Torr. Since the chlorine utilization in the present experiments was far from complete, it is conceivable that high yields could be achieved for high chlorine utilization.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19, SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Final Technical Report, Contract SPC-93-4062, "Development of a Jet-Type Singlet Oxygen Generator"

Submitted by Prof. S. Rosenwaks, Ben-Gurion University of the Negev, on March 22, 1994

Introduction and Summary

Under the framework of the present Contact we have carried out experimental and theoretical investigations of small-scale jet singlet oxygen generators (SOG) of the type described in the Soviet Journal of Quantum Electronics, Vol 21, p. 747, 1991.

The present experimental studies have shown that jet-type generator can operate at high pressures, up to 40 Torr. The maximum $O_2(^1\Delta)$ yield was achieved at 17 Torr; assuming complete chlorine utilization, the yield was 40 ± 15%. The yield dropped at higher pressures, to 25± 10%, at 40 Torr. Since the chlorine utilization in the present experiments was far from complete, it is conceivable that high yields could be achieved for high chlorine utilization.

The theoretical modeling shows that jet-type generators can provide for high yield ($Y > 50\%$) and chlorine utilization ($u_{Cl} = 100\%$) for oxygen pressure up to 50 Torr. The chlorine flow rate should be chosen close to some optimal value which is independent of the pressure. The influence of other parameters (the liquid-jet velocity, the length of the generator, [KOH], the jet number and diameter) on the yield with optimal chlorine flow rate is weak. The heating of the jets due to chemical reaction under our conditions is very small.

Additional experimental and theoretical studies are needed for further development of this generator and, it particular, for the examination of its scalability.

1. Experimental studies

In the course of the Contract period two versions of the jet generator were built. The first was based on a very simple design and served to show that the concept works and to identify possible problems, whereas the second was based on our experience with the first one and on information received from the Russian group of Samara (the authors of the reference mentioned in the Introduction and Summary section).

1.1. Fabrication and experiments with the first jet singlet oxygen generator (SOG)

The schematics of the first jet generator built in our laboratory is presented in Fig. 1. It consists of the following parts:

a. A PVC container for the basic hydrogen peroxide (BHP) solution. The container dimensions are 30x30x30 cm and it is kept at a temperature of -10^{0}C by flowing cooled ethanol (-80^{0}C) through a polyethylene spiral inserted in the container.

b. A jet injector, built from 280 holes of 0.3 mm diam drilled in a plexiglass plate, 8 mm thick.

c. A 100 mm long, 20 mm diam glass tube where interaction between BHP jets and chlorine gas takes place.

d. A container for collecting and recycling the used BHP.

For calculating the $O_2(^1\Delta)$ yield produced in the generator, the pressure and the spontaneous emission of the $O_2(^1\Delta)$ were measured at the generator outlet. Absolute calibration of the yield was obtained using a calorimeter.

The experiments were conducted with BHP prepared from 4 liters of H_2O_2 50% wt. and 3 liters of KOH 47% wt., chlorine flow rate of 5 mmol/s and pressure of 20 Torr. The pressure had to be carefully regulated by means of a teflon valve positioned between the generator outlet and the pump, in order to keep the pressure in the interaction zone high enough to prevent boiling and overflowing of the BHP in this zone. The velocities of the BHP jets and the gaseous chlorine in the interaction zone were 3.5 and 10 m/s, respectively.

1.2. Results and conclusions from the experiments with the first jet generator

The best result obtained in the experiments with the first jet generator is $O_2(^1\Delta)$ yield of ~ 30% (assuming a complete utilization of the chlorine) for chlorine pressure of 20 Torr. Checking carefully the experimental conditions and comparing them with those of the group at Samara (where Prof. Rosenwaks visited in September 93) it was concluded that the two main reasons for the low measured yield, as compared to that of the Russian group, are the following:

a. The BHP jet injectors closest to the exit from the generator should be long enough to "filter" liquid droplets from the gas stream.

b. The pressure of the $O_2(^1\Delta)$ should be reduced (using a valve) as close as possible to the generator outlet to minimize energy pooling (which is extremely detrimental at high pressures).

The results of the experiments with the first jet generator have shown that even in a very short time and minimum expenses it is possible to build and operate a jet generator that although is still very modest in its performance, serves to show that the concept works and to identify the problems that have to be solved to obtain a high performance device.

1.3. Design and fabrication of the new jet SOG

Following the above conclusions a new jet generator was designed and built. The schematics of the new generator is presented in Fig. 2. Not shown in the figure are the PVC containers which are the same as in the previous generator (see Fig. 1). The container for collecting the used BHP solution, which is transferred back to the first container for repeated use, was also cooled by ethanol at -80^{0}C. Fig. 3 is a photograph of the new generator.

The jet injector is composed of 168 stainless syringe needles of 0.5 mm internal diameter "planted" into a teflon plate, 5 mm thick. The needles are arranged in 7 rows; the needles in the row closest to the generator outlet to the valve are long enough to block the outlet (see Fig. 2). The building material of the other parts of the generator is PVC.

1.4. Results and conclusions from the experiments with the new jet generator

The first set of experiments were "cold" experiments where water was injected through the needles to check the shape of the jets. The injection is driven by applying atmospheric pressure on the BHP solution (which is placed above the injectors) while the generator is under vacuum. It was found that homogeneous jets are produced and that their shape is unchanged for a distance of at least 5 cm from the tip of the injectors.

The "hot" experiments were conducted with BHP prepared from 7.5 liters of H_2O_2 50% wt. and 2.5 liters of KOH 47% wt, chlorine flow rate of 1.5 - 8.7 mmol/s and pressure of 6 - 40 Torr inside the generator and 3 - 12 Torr outside the generator (the pressure was controlled by the valve, see Fig. 2). The $O_2(^1\Delta)$ yield was measured via an optical fiber at the exit of the generator valve. The maximum run time of a single experiment was 20 sec. It was found that the generator can work at pressure as high as 40 Torr (higher pressures have not been tried). The maximal $O_2(^1\Delta)$ yield was achieved at 17 Torr; assuming complete chlorine utilization, the yield was $40 \pm 15\%$. The yield dropped at higher pressures, to $25\pm 10\%$, at 40 Torr. Since the chlorine utilization in the present experiments was far from complete, it is conceivable that high yields could be achieved for high chlorine utilization.

Foam and droplet production at the generator outlet during the experiment, which was a major problem in the previous generator, was significantly reduced. Further reduction is highly desirable and, judging from the Samara experiments, could have been achieved if electrical pneumatic valves (which enable to start the chlorine and BHP flows simultaneously) were available.

The present experiments with the new jet generator show that this generator can indeed operate at very high pressure of chlorine. Careful parametric studies, utilizing suitable pneumatic and diagnostic equipment, are needed to find the best operation conditions and to explore the possibilities of scalability.

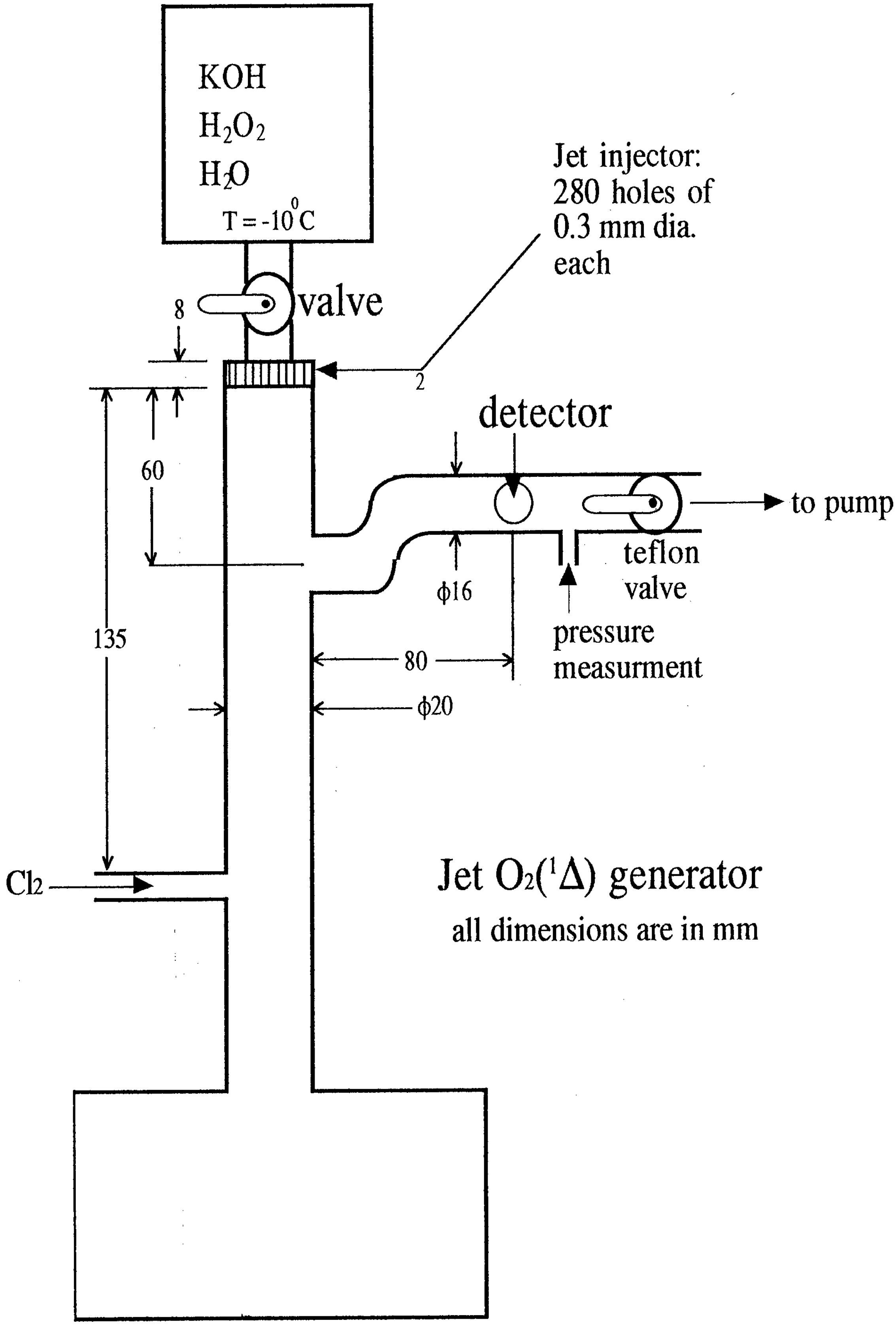

Fig. 1. Schematics of the first jet generator.

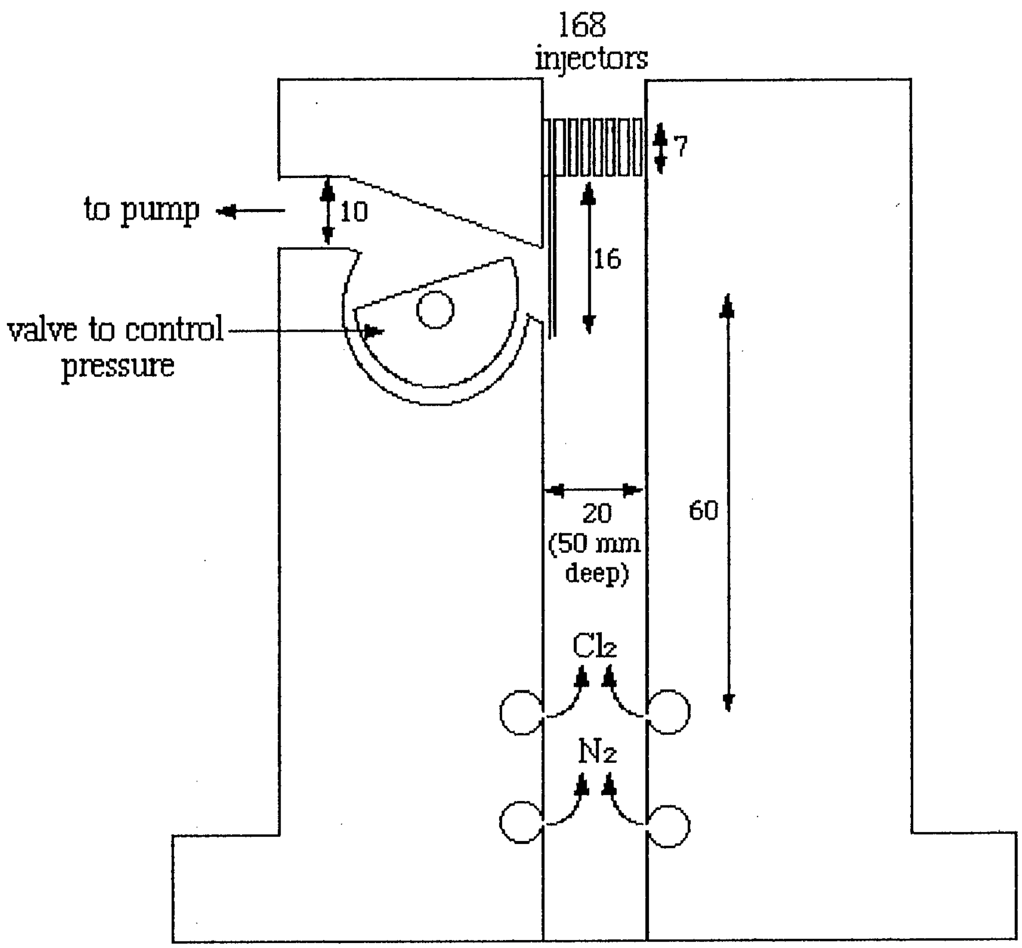

Fig. 2: Schematics of the new jet generator.

All dimensions are in mm.

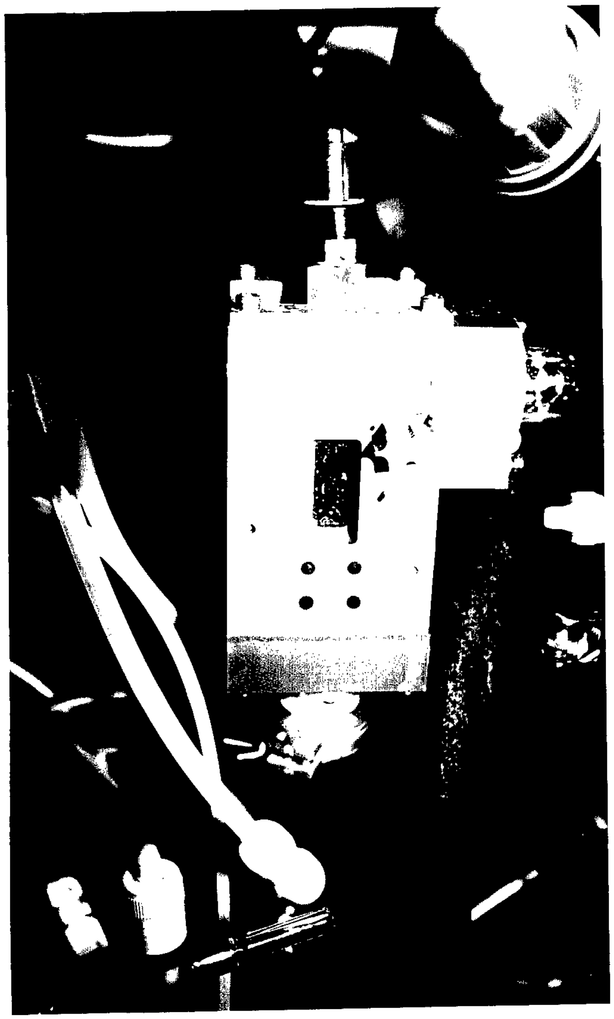

Fig. 3. Photograph of the new jet generator.

2. Theoretical studies

2.1. General considerations

The theoretical studies of the jet-type SOG are based on the results of our recent paper [1] where a general model treating different types of SOGs is developed. We have first studied the case of negligibly small gas-phase quenching. For a SOG of fixed dimensions, for the case where the flows of the BHP jets and Cl_2 are antiparallel, analytic expressions have been derived for the Cl_2 utilization, u_{Cl}, and the $O_2(^1\Delta)$ yield, Y, at the exit of the generator:

for $p > p_{0L}\sqrt{\dfrac{2l_gSD_{Cl}}{U_gK_{Cl}(D_{O2}\tau)^{1/2}}}$,

$$u_{Cl} = \frac{p_{0L}}{p}\sqrt{\frac{2l_gSD_{Cl}}{U_gK_{Cl}(D_{O2}\tau)^{1/2}}},$$

$$Y = \frac{1}{u_{Cl}}\frac{1}{\sqrt{1-\frac{1}{4}\left(\frac{p}{p_{0L}}\right)^2(1-u_{Cl})}}\left\{\tan^{-1}\left[\frac{1}{2}(1+u_{Cl})\frac{p}{p_{0L}\sqrt{1-\frac{1}{4}\left(\frac{p}{p_{0L}}\right)^2(1-u_{Cl})}}\right] - \tan^{-1}\left[\frac{1}{2}(1-u_{Cl})\frac{p}{p_{0L}\sqrt{1-\frac{1}{4}\left(\frac{p}{p_{0L}}\right)^2(1-u_{Cl})}}\right]\right\}, \tag{1}$$

for $p < p_{0L}\sqrt{\dfrac{2l_gSD_{Cl}}{U_gK_{Cl}(D_{O2}\tau)^{1/2}}}$,

$$u_{Cl} = 1, \quad Y = \frac{p_{0L}}{p}\tan^{-1}\left(\frac{p}{p_{0L}}\right), \tag{2}$$

where p_{0L} is given by Eq.(50) of Ref. [1], p is the partial pressure of Cl_2, l_g is the length of the generator, D_Z and K_Z are the diffusion coefficient and Henry constant, respectively, of the Z component, τ is the $O_2(^1\Delta)$ quenching time in the liquid and S is the specific gas/liquid interfacial area per unit volume. S can be expressed through the diameter of the jet, d_j, and that of the generator, d_g, and the number of jets, N_j, as $S = 4d_jN_j/d_g^2$. It should be noted that Eq. (1) for Y differs from that obtained in [1] because here the Cl_2 is not assumed to be completely utilized.

2.2. Results and comparison with experiments

In order to take into account the gas-phase quenching of $O_2(^1\Delta)$, a numerical code has been developed based on the simplified model of Ref. [1] which calculates u_{Cl} and $Y_{measured} \equiv Yu_{Cl}$ (i.e. the yield normalized to chlorine number density at the generator inlet). The calculation was done for the best conditions of Ref. [2] (p = 30 Torr, chlorine flow rate of 5.8 mmol/s (corresponding gas velocity U_g = 10.5 m/s) and liquid-jet velocity U_l = 6 m/s). The calculation gives (the conditions of Eq (2) apply here) u_{Cl} = 1 and $Y_{measured}$ = 0.56. The value of $Y_{measured}$ is close to that found in the experiment, ~ 0.6 [2], although u_{Cl} is around 0.95 under the conditions of [2].

The very good agreement between the experimental and theoretical results indicates that the model can predict the behavior of the generator for different conditions of operation. Thus, parametric studies have been carried out of the behavior for different gas and liquid velocities, jet diameters and KOH concentration.

In these studies the gas and liquid velocities as well as the gas pressure were varied, whereas the dimensions of the generator and jet diameter were fixed and equal to those of our first jet generator described above. S was equal to 8.4 cm^{-1} and the length of the generator to 10 cm. The liquid solution was the same as usually used in our laboratory; $[HO_2^-] = 3.3M^{-1}$ and T = 263 K were used for the calculations. The results of the calculations are shown in Figs. 4-8.

Fig. 4 shows the chlorine utilization u_{Cl}, the yield Y and $Y_{measured} \equiv Yu_{Cl}$ as a function of the gas velocity U_g for different pressures p and liquid velocity U_l = 6 m/s. Y and $Y_{measured}$ show maxima (especially pronounced for $Y_{measured}$) whereas u_{Cl} is constant and equal to 1 until the end of the reaction zone reaches the end of the generator and then falls with the rise of U_g. The maximum value of Y is achieved exactly at the point where u_{Cl} starts to fall. Therefore this maximum corresponds to a velocity U_g for which the chlorine is completely utilized exactly at the end of the generator. Both u_{Cl} and Y fall with the rise of the pressure (see more details in Fig. 7).

Fig. 5 shows the dependencies of u_{Cl} and Y on the liquid velocity for different gas velocities and fixed pressure, p = 30 Torr. Once again, Y shows a maximum, whereas u_{Cl} rises with the rise of

U_l (until the maximum value $u_{Cl} = 1$ is reached). The maximum value of Y again is achieved when the chlorine is completely consumed at the end of the generator.

Nonmonotonous dependencies of Y on $U_{g,l}$ are not trivial. They can be explained by the spatial distributions of Y and the dimensionless concentration of Cl_2, $n_{cl} \equiv [Cl_2]/[Cl_2]_0$ (the subscript $_0$ denotes the value at the generator inlet), inside the generator shown in Fig. 6 for different values of U_g and fixed $p = 30$ Torr and $U_l = 6$ m/s. It is seen that Y increases with x (measured from the point of Cl_2 injection) up to the point where the Cl_2 is completely utilized and then decreases. The increase of Y is due to the fact that for antiparallel directions of the gas and liquid flows the gas flowing along the generator reacts with less and less depleted liquid reactant, which results in larger values of Y. The decrease of Y after the completion of the gas/liquid reaction is due to the gas-phase quenching of $O_2(^1\Delta)$. Fig. 6 shows that as U_g increases from 8 to 12 m/s, the end of the reaction zone approaches the end of the reactor, resulting in an increase of the yield at the end of the SOG. Further increase of U_g results in a decrease of the chlorine utilization u_{Cl} and hence of Y at the end of the SOG. This explains the nonmonotonous dependence of Y on U_g. The dependence of Y on U_l can similarly be explained.

Fig. 7 shows the pressure dependence of u_{Cl} and Y for different values of U_g where $U_l = 6$ m/s. For high U_g both u_{Cl} and Y decrease as the pressure increases. However, for low U_g, Y(p) is nonmonotonous and has a local maximum for a pressure which brings the end of the reaction zone to coincide with the end of the SOG.

Figs. 4 and 5 show that the yield Y does not always increase with liquid or gas velocity. In order to achieve the increase of Y one has to increase U_l and U_g simultaneously in such a way that the length of the gas/liquid reaction zone is equal to the length of the SOG. To this end, as is shown in Ref. [1], the gas velocity U_g should be proportional to $(U_l)^{1/2}$. Fig. 8 shows Y as a function of U_l ($p = 30$ Torr) in the case when U_l and U_g increase simultaneously, providing for the optimal conditions where $u_{Cl} \approx 1$. One can see that the maximum yield $Y \sim 0.8$ can be achieved for $U_{g,l} \sim$ 20 m/s.

Some of the above conclusions are in qualitative agreement with the experiments made recently in

Samara on the jet-type SOG with high U_l (up to 20 m/s) and U_g (up to 30 m/s) [3]. In particular, in experiments with $U_g = 10$ m/s, Y decreased as U_l increased from 5 to 20 m/s, which is in agreement with the dependence presented by the dashed curve in Fig. 5. The authors of Ref. [3] claim also that the increase of Y is only achieved with simultaneous increase of U_l and U_g which also agrees with our conclusions.

2.3. Simple engineering formulas for estimating optimal parameters

It is possible at this point to derive simple engineering formulas to estimate the optimal parameters of the generator. First of all it is convenient to express u_{Cl} in terms of the chlorine flow rate nCl which can be easily controlled:

$$u_{Cl} = (L\, D_{HO_2^-}\, U_l/\pi)^{1/2} \frac{[HO_2^-]S}{(nCl/A)}, \tag{3}$$

where A is the generator cross section. Eq. (3) (which is correct only for $u_{Cl} \leq 1$) shows that for given generator and solution the chlorine utilization depends only on nCl and is independent of the pressure. As mentioned above, the maximum yield is achieved for $u_{Cl} = 1$. Therefore the optimal nCl is given by

$$nCl = (l_g\, D_{HO_2^-}\, U_l/\pi)^{1/2}[HO_2^-]S\ A\,. \tag{4}$$

This optimal nCl (which is independent of the pressure) can be found for any particular generator. If the gas phase quenching is negligibly small, the corresponding optimal Y is given by

$$Y = \left(\frac{p_{ch}}{p}\right)^{1/2} \mathrm{tn}^{-1}\left(\frac{p}{p_{ch}}\right)^{1/2},$$

$$p_{ch} = \frac{K_{Cl}\,[HO_2^-]\,kT}{2}\left(\frac{D_{HO_2^-}\, D_{O_2}\, \tau\, U_l}{D_{Cl}^2\, \pi\, l_g}\right)^{1/2}. \tag{5}$$

The pressure dependence of Y differs from that given by Eq. (2) because this equation is derived under the assumption that U_g = const, whereas Eq. (5) is correct for nCl = const. The pressure dependence in (5) is weaker than in (2). Eq.(5) is the upper estimate for the yield. Its validity improves as S rises and hence the influence of the gas phase quenching decreases (Ref. [1]).

Nevertheless, it can give an idea about the dependence of Y on different parameters. It is seen that the optimal Y is independent of S and hence of the hole number and diameter. The dependencies on the other parameters, l_g, U_l, $[HO_2^-]$, are also weak, e.g., Y approximately is proportional to $U_l^{1/4}$. Therefore, the optimal yields of the jet generators with different geometries and liquid solution are close to each other. The dominant factor is nCl.

The above properties are illustrated in the case of the above-mentioned new generator, with rectangular cross section, built and operated in our laboratory. For this generator S was equal to 3.5 cm^{-1} (168 jets with a diameter of 0.5 mm each) and the length of the generator to 6 cm, both values being less than those in the case of our first generator. A jet velocity $U_l = 10$ m/s is assumed. Fig. 9 shows the pressure dependence of the yield for different nCl. The curves are smoother than those shown in Fig. 7 because, as mentioned above, with constant nCl the chlorine utilization for any curve is constant. The optimal value of nCl is close to 6 mmol/s (for higher nCl the values of u_{Cl} are less than 1 and hence $Y_{measured}$ falls). This value is very close to that found from Eq.(4): nCl = 6.4 mmol/s. At the same time the optimal yield is much less than the theoretical estimate (5) also presented in Fig. 9. The reason for such a disagreement is that our new generator has small gas/liquid interfacial area S and hence the effect of gas-phase quenching is strong. Calculations which are not presented here show that for the old generator with bigger S the agreement between analytic and numerical calculations is much better.

2.4. Further modeling results and conclusions

Dependencies of Y and u_{Cl} on nCl are shown in Fig. 10. It is seen that in order to achieve the best operation conditions, i.e., maximum yield and complete chlorine utilization ($u_{Cl} = 1$), nCl should be close to 6 mmol/s. For large deviations from this optimal value, either Y or u_{Cl} strongly decreases.

Fig. 11 shows the pressure dependence of Y for different numbers of jets. Each curve corresponds to the optimal nCl. The dependence of Y on the jet number is very weak, which is in agreement with the above analytic results (Eq. (5)). Actually, the only parameter in Eqs. (4) and (5) containing the jet number is S which does not affect Y (see Eq. (5)). Calculations which are not presented here show that with a fixed liquid velocity the optimal Y is also weakly dependent on

the jet diameter.

Fig. 12 shows the pressure dependence of Y for three different BHP solutions. The first solution is with [KOH] = 2.9 M (this is used in our experiments with jet SOGs), the second with [KOH] = 5 M (used in our bubble type generator) and the third with [KOH] = 7.2 M (used in the rotating disk generator [4]). The diffusion coefficients and Henry constant were calculated according to [5]. [KOH] is seen to have a small effect on the yield which also is in agreement with Eq. (5). Actually, as [KOH] rises K_{Cl} (the Henry constant) falls and their product appearing in the expression for p_{ch} in (5) does not appreciably change.

Calculations of the jet temperature also are performed. The thermal conductivity equation in the jet was solved with boundary conditions in the surface taking into account the heat release in the chemical reactions. The dependence of the temperature in the surface (the temperature in the bulk of the liquid is lower) on the jet velocity for different jet diameters is shown in Fig. 13. The initial temperature of the jet is assumed to be 263 K. For the conditions of the new generator the heating is very small even in the case of very low U_l. The increase of the jet temperature becomes important only for jets with a diameter less than 0.1 mm. However, for such small jets other effects disturbing the generator operation are more significant (jet break up and decrease of U_l, see Ref. [6]). Calculations of the water vapor pressure at the exit from the generator show that this pressure is almost equal to the saturated vapor pressure for the temperature of the liquid. For parameters of the new generator this pressure is less than 2 Torr and makes up less than 10% of the oxygen pressure.

In conclusion, the theoretical modeling shows that jet-type generators can provide for high yield ($Y > 50\%$) and chlorine utilization ($u_{Cl} = 100\%$) for oxygen pressure up to 50 Torr. The chlorine flow rate should be chosen close to some optimal value which is independent of the pressure. The influence of other parameters (U_l, l_g, [KOH], jet number and diameter) on the yield with optimal chlorine flow rate is weak. The heating of the jets due to chemical reactions under our conditions is very small.

References

[1] B. D. Barmashenko and S. Rosenwaks, J. Appl. Phys. **73**, 1598 (1993).

[2] M.V. Zagidullin et al, Sov. J. Quantum Electron. **21**, 747 (1991).

[3] V.N. Azyazov et al, "Jet Singlet Oxygen Generator up to 100 Torr", unpublished.

[4] G. M. Harpole et al, AIAA **92-3006**.

[5] O. Aharon et al, J. Appl. Phys. **70**, 5211(1991).

[6] Charmaine C. Franck, "COIL Jet Generator Characterization", Quarterly report, December 1993, DLR.

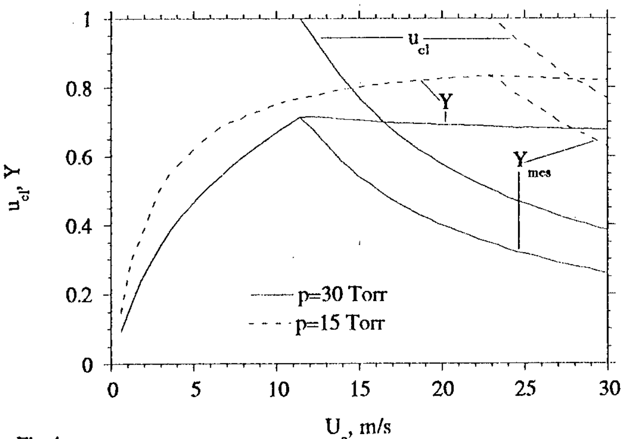

Fig.4

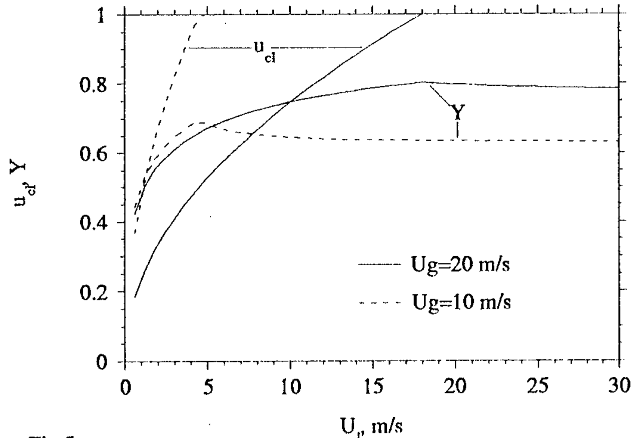

Fig.5

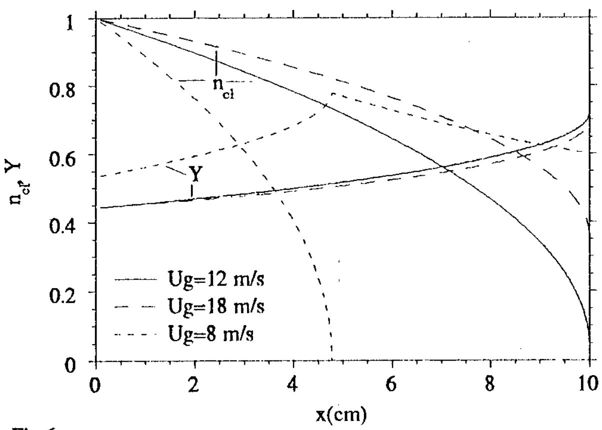

Fig.6

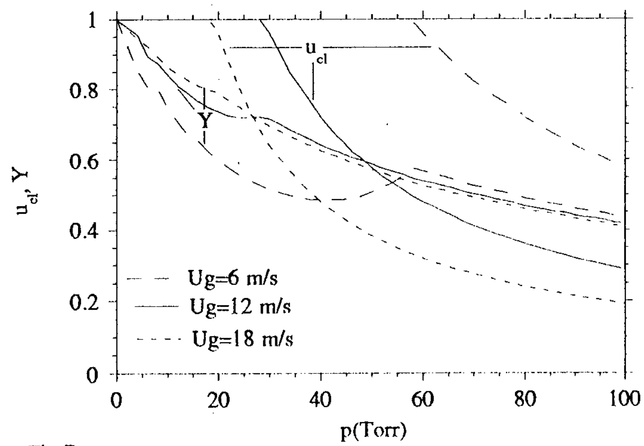

Fig.7

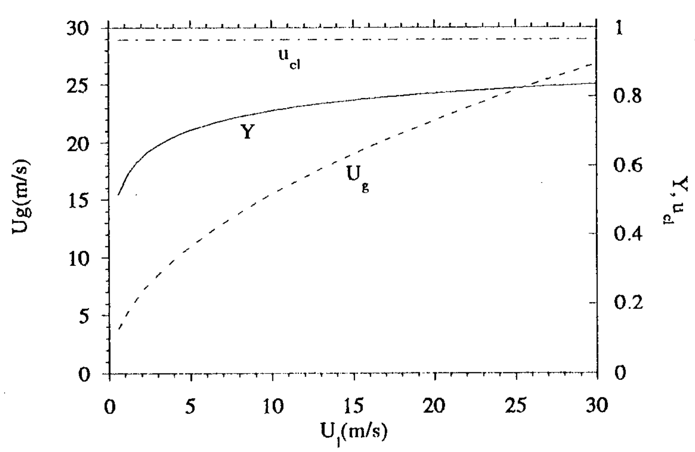

Fig.8

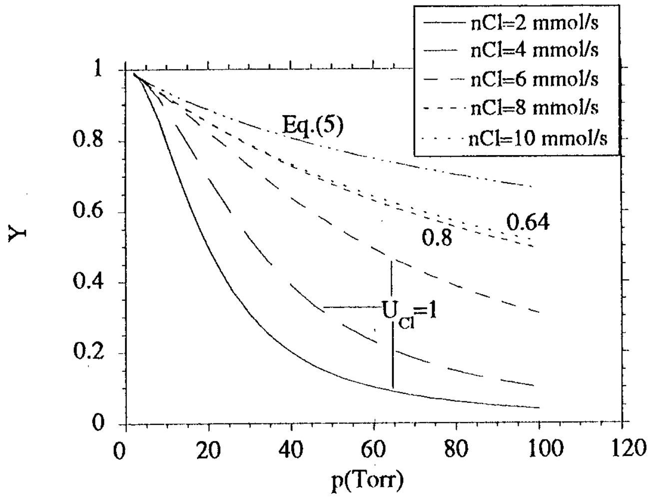

Fig.9

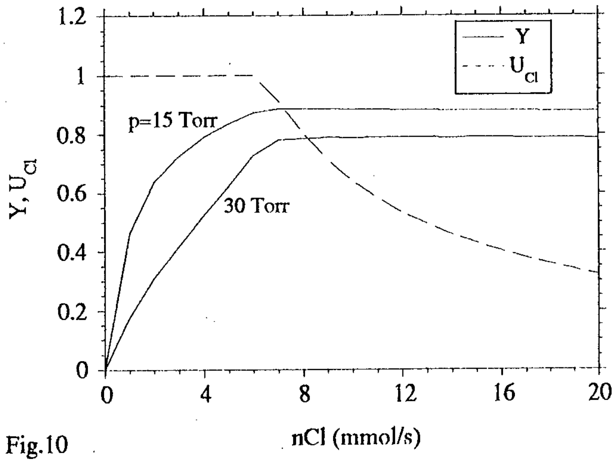

Fig.10

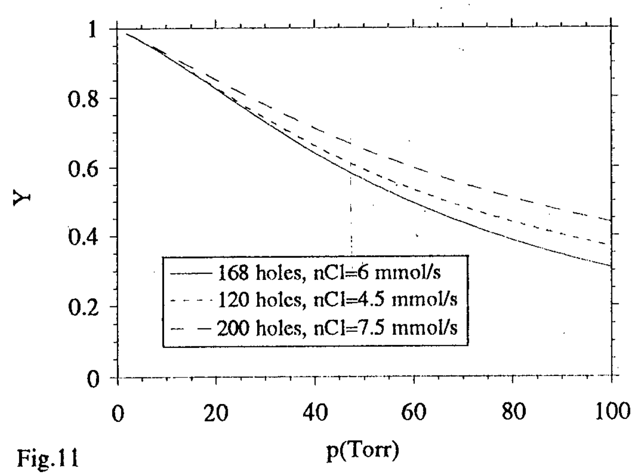

Fig.11

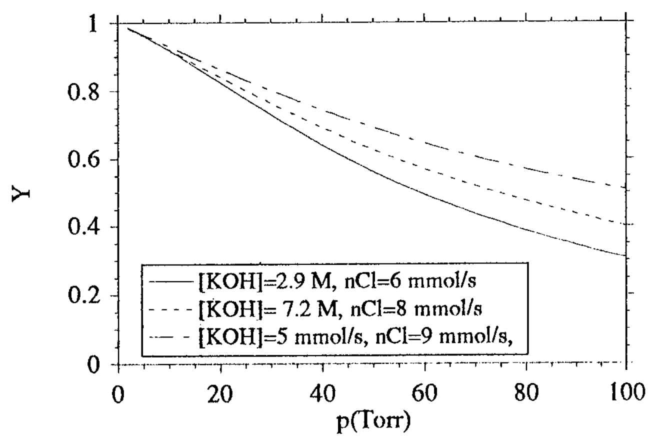

Fig.12

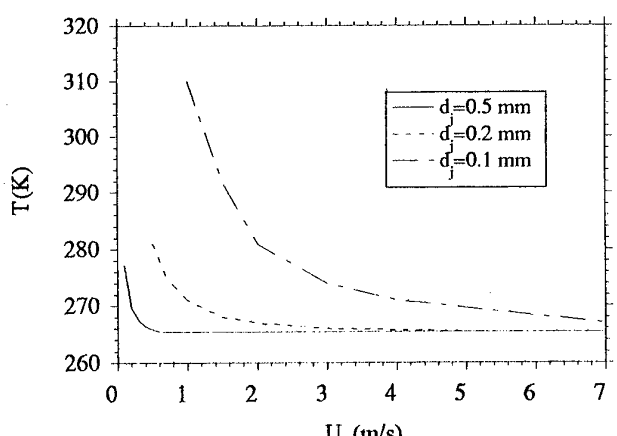

Fig. 13